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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the charging and discharging control device which can prevent degradation of the cell capacity of a nonaqueous electrolyte secondary battery especially about the charging and discharging control device of the nonaqueous electrolyte secondary battery using the occlusion and discharge of lithium.

[0002]

[Description of the Prior Art]While the miniaturization of a cellular phone, a personal computer, etc. progresses, in the field of communication equipment, an information related equipment, etc., A rechargeable battery with an energy density high as a power supply of these apparatus can ask, and it is becoming in use to use the nonaqueous electrolyte secondary battery using the occlusion and the discharge phenomenon of lithium and what is called a lithium secondary battery \*\*\*\* and now. On the other hand, also in the field of a car, from the resources problem and the environmental problem, development of an electromobile is hurried and the lithium secondary battery is expected as a power supply used for an electromobile.

[0003]The good cycle characteristic that cell capacity does not deteriorate by the charge and discharge repeated, either is required not only of a lithium secondary battery but of a rechargeable battery. In order that in the case of a lithium secondary battery various causes of cycle degradation may be considered and may raise this cycle characteristic, improvement of the negative electrode active material by the partial substitution of a composing element, improvement of the positive active material by the superiors for crystallinity, surface ornamentation, etc., etc. are energetically advanced in the cell industry. The improvement to nonaqueous electrolyte, a separator, etc. is also made and the cycle characteristic of a [ not only a positive-and-negative-poles active material but / the conducting material in positive and negative poles, a binder, etc. ] has also been improving considerably in recent years.

[0004]However, under the present circumstances, it cannot be said to be that whose cycle characteristic improved even on the still satisfying level, but a cell reaction is especially activated by causes, such as a viscosity decrease of nonaqueous electrolyte, in the use under an elevated temperature, and degradation of the cell capacity by repetition of charge and discharge is intense. If it takes being neglected on the outdoors into consideration when using a lithium secondary battery as a power supply for electromobility is assumed, it is necessary for a good cycle characteristic to be maintainable also in an about 60 °C elevated temperature.

[0005]Generally in the lithium secondary battery, lithium transition metal multiple oxides, such as  $\text{LiCoO}_2$ , are used as positive active material. the major factor of the cycle degradation of cell capacity -- the charge and discharge of a cell -- positive active material -- in connection with occlusion and being emitted, the lithium transition metal multiple oxide itself repeats [ lithium ] expansion and contraction to this lithium transition metal compound \*\*\*\*, and it is in a crystal structure collapsing.

[0006]In the conventional charge and discharge control, the charge and discharge managed with the closed circuit upper limit voltage and closed circuit lower limit voltage at the time of charge and discharge are performed so that a nonaqueous electrolyte secondary battery may not serve as overcharge or overdischarge. Only by however, the regulation by this closed circuit upper limit voltage and closed circuit lower limit voltage. When a nonaqueous electrolyte secondary battery is operated under an elevated temperature, Since a chargeable and dischargeable field spreads reversibly and the charge and discharge of big capacity are performed, occlusion and the lithium emitted will increase to the lithium transition metal multiple oxide which is positive active material, and the lithium transition metal multiple oxide itself will repeat big expansion and contraction. In the conventional charging and discharging control device which is not taking into consideration use in a broad temperature region, collapse of the crystal structure of a lithium transition metal multiple oxide is not avoided, but has not come [ therefore, ] to prevent degradation of the cell capacity of a nonaqueous electrolyte secondary battery.

[0007]

[Problem(s) to be Solved by the Invention]this invention person noted being able to prevent degradation of cell capacity from the side of use of a nonaqueous electrolyte secondary battery, i.e., the point of a charging and discharging method. And also in use in a broad temperature region, as a result of repeating various experiments, the knowledge that cell capacity hardly deteriorated lithium by occlusion and making it emit was acquired to such an extent that the crystallinity of the lithium transition metal multiple oxide which is positive active material did not fall.

[0008]In [ this invention is based on this knowledge and ] the charge and discharge of a nonaqueous electrolyte secondary battery, Restrict a charge-and-discharge field by monitoring

charge-and-discharge quantity of electricity, and collapse of the crystal structure of the lithium transition metal multiple oxide which is positive active material is prevented, It is making to provide the charging and discharging control device which does not degrade most cell capacity by the charge and discharge repeated, especially the charge and discharge under an elevated temperature, either into the technical problem.

[0009]

[Means for Solving the Problem]A charging and discharging control device of a nonaqueous electrolyte secondary battery of this invention, It is a charging and discharging control device of a nonaqueous electrolyte secondary battery which has the anode which used a lithium transition metal multiple oxide as positive active material, A charging state primary detecting element which detects charge-and-discharge quantity of electricity of said rechargeable battery, integrates detected charge-and-discharge quantity of electricity to a standard charging state, and detects a charging state of this rechargeable battery, When this charging state detected by this charging state primary detecting element turns into a setting-out maximum charging state, charge to this rechargeable battery is stopped, And it has a charge-and-discharge control section which stops discharge to this rechargeable battery when this charging state detected by this charging state primary detecting element turns into a setting-out minimum charging state, Difference capacity of this rechargeable battery of this setting-out maximum charging state and this setting-out minimum charging state is characterized by being 50% or less of the theoretical capacity of this anode.

[0010]A nonaqueous electrolyte secondary battery which is the target of control uses a lithium transition metal multiple oxide for positive active material, and occlusion and discharge of lithium are done from this multiple oxide in connection with charge and discharge. If the state where all lithium that existed in positive active material at the beginning was emitted is assumed to be a "full charge state" and all lithium that existed in positive active material at the beginning assumes the state where occlusion is carried out to be an "empty charging state", Difference capacity of a "full charge state" and an "empty charging state" turns into capacity equivalent to positive-active-material theoretical capacity. A "charging state" of a nonaqueous electrolyte secondary battery which this control device detects means what lithium in positive active material remains, and it becomes a value which shows a ratio of lithium which remains in positive active material to anode theoretical capacity. And if it charges to a rechargeable battery in a certain "charging state", lithium will be emitted from the inside of positive active material, a ratio of lithium which remains in positive active material will decrease, and a "charging state" will tend toward a "full charge state." Contrary to this, if it is made to discharge, a ratio of lithium which exists in positive active material will increase, and a "charging state" will tend toward an "empty charging state."

[0011]When one lithium atoms ionize, and when one lithium ion turns into a lithium ion,

peculiar quantity of electricity is exchanged with an anode. Therefore, a "charging state" of a rechargeable battery can always be monitored by monitoring quantity of electricity by which charge and discharge are carried out to a rechargeable battery, and always integrating quantity of electricity accompanying charge and discharge to a "charging state" used as a certain standard. Since quantity of electricity accompanying charge and discharge integrates with charging current and discharge current about charging time and a charging time value, it always monitors a charge and discharge current, and integrates with this about charge and discharge time, A "charging state" of a rechargeable battery can always be monitored by integrating to a "charging state" used as a certain standard.

[0012]If charge and discharge control by a charging and discharging control device of a nonaqueous electrolyte secondary battery of this invention is typically shown from a charging state of a rechargeable battery, it will become like drawing 1. Temperature on which a cell is put by vertical axis is shown to a horizontal axis in a "charging state" of a rechargeable battery by drawing 1. A charging state makes a "full charge state" 100%, makes an "empty charging state" 0%, and has expressed it as percentage. A "charging state" has a "lithium anode residual ratio" ("capacity equivalent to lithium which remains in positive active material"/"anode theoretical capacity") similarly expressed in units of percentage, and a relation of "charging state" + "lithium anode residual ratio" =100.

[0013]Generally, a nonaqueous electrolyte secondary battery has a "overcharge field" in the "full charge state" side, and has an "overdischarge field" in the "empty charging state" side. In order that a "overcharge field" and a "overdischarge field" being occlusion and a field which cannot be emitted about lithium reversibly, and performing charge and discharge in this range may cause cell destruction and remarkable performance degradation, Normal use is not carried out, but generally, cell voltage (short circuit voltage) of a cell is managed, and when it becomes predetermined cell voltage, charge and discharge are stopped. Charge and discharge are carried out in this field by making a staging area except this a "overcharge field" and an "overdischarge field" into a "reversible chargeable and dischargeable field." A "reversible chargeable and dischargeable field" has a close relation to temperature on which a cell is put, and becomes large gradually by factors, such as a viscosity decrease of nonaqueous electrolyte, with a rise of battery temperature. In a conventional control method managed only with cell voltage, with a rise of battery temperature, more lithium will repeat occlusion and discharge to positive active material, and capacity deterioration of a rechargeable battery will become remarkable.

[0014]As mentioned above, cell voltage sets up a "setting-out maximum charging state" used as a maximum, and a "setting-out minimum charging state" used as a minimum independently, and charge and discharge control by a charging and discharging control device of this invention controls to repeat charge and discharge in a "control charge-and-discharge field"

across which it faced among both. Thus, when a rechargeable battery is placed by what kind of temperature by a rechargeable battery's carrying out charge-and-discharge quantity of electricity detection, and monitoring a "charging state" of a rechargeable battery, even if it is, positive active material can be made to always do occlusion and discharge of lithium of quantity below fixed. [ make / get it blocked and / this "control charge-and-discharge field" and / and / into 50% or less of anode theoretical capacity / difference capacity of a "setting-out maximum charging state" and a "setting-out minimum charging state" ] Collapse of a crystal structure of a lithium transition metal multiple oxide which is positive active material is controlled, and it makes it possible to prevent degradation of cell capacity of this nonaqueous electrolyte secondary battery.

[0015]Anode theoretical capacity is uniquely determined by a kind of positive active material which a nonaqueous electrolyte secondary battery which is the target of control uses, and its cathode active material volume. About an antecedent basis of making a "control charge-and-discharge field" into 50% or less of anode theoretical capacity, it obtains by experiment, and a paragraph of a next example explains this experiment in detail.

[0016]In a charging and discharging control device of this invention, a standard charging state set part which sets a charging state which detects open-circuit voltage of this rechargeable battery at the time of non-charge and discharge of a rechargeable battery, and is converted from detected open-circuit voltage to a standard charging state can also be added. A "charging state" of a maximum of a "reversible chargeable and dischargeable field" at prescribed temperature of a certain stage and a minimum, a "charging state" which integrated charge-and-discharge quantity of electricity from a rechargeable battery manufacture time, etc. can be used for a "standard charging state" used as a standard of detection of a "charging state." However, after "standard charge-and-discharge state" setting out, while repeating charge and discharge, a gap may be produced between actual "charging states" by leak in a circuit of a charge and discharge current, etc. Therefore, it is desirable to reset up a "standard charging state" to arbitrary or predetermined timing. This standard charging state set part functions as a "charging state" which integrates and detects this charge and discharge current collateralizing that actual "charging state" is shown.

[0017]Relation between open-circuit voltage of a nonaqueous electrolyte secondary battery and a charging state is shown in drawing 2. In a nonaqueous electrolyte secondary battery which used as positive active material a lithium transition metal multiple oxide which is the target of control of this control device, open-circuit voltage when not performing charge and discharge is a value depending on a "charging state", and shows a fixed relation by composition of a rechargeable battery. Therefore, by measuring open-circuit voltage at the time of this standard charging state set part and non-charge and discharge, from open-circuit voltage of the rechargeable battery for which it asked beforehand by examination etc., and a

relation with a "charging state", a "charging state" of the rechargeable battery in the time is grasped, and this is set up as a "standard charging state." It becomes possible to detect very exact "charging state" by adding this standard charging state set part to a charging and discharging control device of this invention.

[0018]

[Embodiment of the Invention]Below the embodiment of the charging and discharging control device of this invention is described, and the embodiment of the nonaqueous electrolyte secondary battery which is subsequently the target of control of the charging and discharging control device of this invention is described.

<Charging and discharging control device> The key map of the charge-and-discharge control system constituted by drawing 3 including the charging and discharging control device which controls a nonaqueous electrolyte secondary battery and its rechargeable battery is shown. Since the charge-and-discharge control system shown in drawing 3 is only one illustrated embodiment, the charging and discharging control device of this invention is not limited to this charge-and-discharge control system.

[0019]The charge-and-discharge control system shown in drawing 3 consists of the nonaqueous electrolyte secondary battery 10, the load 20 and the charging power 30 which are connected to the rechargeable battery 10, the charge-and-discharge switcher 40 which changes the charge and discharge to the rechargeable battery 10, and a charging and discharging control device which performs control of charge and discharge. The charging and discharging control device comprises the charging state primary detecting element 50 which detects the charging state of the rechargeable battery 10, the charge-and-discharge control section 60 which stops charge and discharge, and the standard charging state set part 70 which sets up the standard charging state of the rechargeable battery 10. The charge and discharge current detector 51 which detects the current value of the discharge current discharged from the charging current and the rechargeable battery 10 with which the charging state primary detecting element 50 is charged by the rechargeable battery 10, It integrates with the charge and discharge current outputted from the charge and discharge current detector 51 about charge and discharge time, is considered as charge-and-discharge quantity of electricity, and consists of the integrator 52 which integrates this charge-and-discharge quantity of electricity to a standard charging state, and is outputted as a charging state value.

[0020]The charge-and-discharge control section 60 compares the setting-out maximum charging state value and setting-out minimum status value which were inputted with the charging state value outputted from the charge-and-discharge primary detecting element 50, It is arranged between the comparator 61 which outputs the signal of the charge ON and OFF, and the signal of the discharge ON and OFF, and the load 20 and the charging power 30 and the rechargeable battery 10, and consists of the charge and discharge switch 62 for continuing

and stopping the charge to the rechargeable battery 10, and the discharge from the rechargeable battery 10. The open-circuit voltage detector 71 in which the standard charging state primary detecting element 70 detects the open-circuit voltage of the rechargeable battery 10, It consists of the conversion machine 72 which is converted into the charging state of the rechargeable battery 10, and is outputted to the charging state primary detecting element 50 by making this reduced property into a standard charging state value with the relating data which made the open-circuit voltage value outputted from the open-circuit voltage detector 71 memorize beforehand.

[0021]The integrator 52, the comparator 61, and the conversion machine 72 may perform charge and discharge control among the components of these charging and discharging control devices, using the computer for control, etc. as one. When this charge-and-discharge control system is equipped or carried in actual apparatus or vehicles, when carried in an electromobile, the load 20 serves as a motor for a vehicles drive, and the charging power 30 serves as a regeneration output from a battery charger or a vehicles drive motor, for example. Alternative connection between the rechargeable battery 10, and the load 20 and the charging power 30 is made via the charge-and-discharge switcher 40, and it is performed by operating the charge-and-discharge switcher 40 by control device with this another charging and discharging control device which is not shown in drawing 3.

[0022]This charging and discharging control device aims at performing charge and discharge in the control charge-and-discharge field which becomes 50% or less of the anode theoretical capacity of the rechargeable battery 10, as mentioned above. The parameter of the foundations managed in this charge and discharge control is a charging state value showing the charging state of the rechargeable battery 10. Since a charging state value makes an empty charging state 0% and can evaluate a full charge state as 100% as mentioned above, it expresses this % with the following explanation as a unit for convenience.

[0023]First, the setting-out maximum charging state value for determining a control charge-and-discharge field and a setting-out minimum charging state value are inputted into the comparator 61. For example, what is necessary is just to input the value from which the difference capacity will be 50% or less like 20% about 70% and a setting-out minimum charging state value in a setting-out maximum charging state value. It may be an input method which determines the setting-out minimum charging state value or setting-out maximum charging state value which inputs either one of a setting-out maximum charging state value or a setting-out minimum charging state value, inputs the value of difference capacity, i.e., a control charge-and-discharge field, with the value used as 50% or less, and corresponds by an operation.

[0024]The charge and discharge current detector 51 in the charging state primary detecting element 50 can measure the charge and discharge current to the rechargeable battery 10, and

a what is called direct-current type ammeter is just used for it. However, it is necessary to be what can detect whether it is current of a charging direction, or it is current of a discharge direction. What is necessary is to continue measuring a charge and discharge current and just to continue outputting the charge and discharge current value and direction of charge and discharge to the integrator 52.

[0025]The integrator 52 in the charging state primary detecting element 50 integrates with and integrates the charging current value of the charge and discharge current detector 51 about charge and discharge time to the standard charging state value in the standard charging state at the predetermined time, and detects the charging state of the rechargeable battery 10. Since the integral value about the charge and discharge time of a charge and discharge current will turn into a value which shows the electric capacity by which charge and discharge are carried out if the charging state value in this time of the rechargeable battery 10 is set to  $x$  (%), The value which  $x$  (ed) electric capacity integrated with and calculated with the anode theoretical capacity of the rechargeable battery 10 will show charging state variation  $\Delta x$  [ of the rechargeable battery 10 ]  $x$  (%). If the standard charging state value in a predetermined time is made into  $x_0$  (%) and this value is made to memorize, To this standard charging state value  $x_0$  (%), if it is a charging direction, above-mentioned charging state variation  $\Delta x$  (%) will be added, and charging state  $x$  (%) and  $(x=x_0+\Delta x)$  of the rechargeable battery 10 in this time can be detected by subtracting, if it is a discharge direction. When the standard charging state in a predetermined time sets in this charging and discharging control device the rechargeable battery of a certain charging state measured preparatorily, can set it up with that charging state of a certain, but. It is desirable to have a reference state value outputted from the standard charge-and-discharge state set part 70 at the time of the non-charge and discharge explained later, and to set up, whenever it is outputted.

[0026]The charging state value  $x$  (%) outputted from the charging state primary detecting element 50 is inputted into the comparator 61 in the charge-and-discharge control section 60. The comparator 61 is always comparing the charging state value inputted, and the above-mentioned setting-out maximum charging state value and a setting-out minimum charging state value. And if  $x$  (%) and  $x_H$ , and a setting-out minimum status value are made into  $x_L$  (%), the comparator 61 a setting-out maximum charging state value, The signal of the discharge OFF is outputted [ at the time of  $x \leq x_H$  / a charge ON signal / a charge OFF signal ] for a discharge ON signal to the charge and discharge switch 62, respectively at the time of  $x < x_L$  at the time of  $x \geq x_L$  at the time of  $x > x_H$ .

[0027]The charge and discharge switch 62 in the charge-and-discharge control section 60, It consists of a charge switch which opens and closes between the rechargeable battery 10 and



the charging power 30, and a discharge switch which opens and closes between the rechargeable battery 10 and the loads 20, and each switch opens and closes according to the above-mentioned charge ON and OFF signal, and discharge ON and the OFF signal which are outputted from the comparator 61. That is, the charging state value  $x$  as which the charge and discharge switch 62 expresses the charging state of the rechargeable battery 10. It will be in the state where in  $x_L \leq x \leq x_H$  the charge switch and the discharge switch were closed so that it might be chargeable and dischargeable, the charge switch opened so that charge might be impossible in  $x > x_H$ , and the discharge switch opened so that discharge might be impossible, when it was  $x < x_L$ . Thus, when the charge switch 62 operates, the rechargeable battery 10, in the control charge-and-discharge field between a setting-out maximum charging state value and a setting-out minimum charging state value, it is got blocked, and it is the difference capacity of a setting-out maximum charging state and a setting-out minimum charging state, and is controlled chargeable and dischargeable within the limits of 50% or less of anode theoretical capacity.

[0028]Subsequently, the standard charging state set part 70 is explained. In a non-charge-and-discharge state, for example, the state where the rechargeable battery 10 is connected to neither the charging power 30 nor the load 20 by the charge-and-discharge switcher 40, the open-circuit voltage detector 71 in the standard charging state set part 70 detects cell voltage. When the closed circuit state, i.e., charge and discharge, is being performed, cell voltage is influenced by charge and discharge current density, the environmental temperature on which the rechargeable battery is put, etc., and since cell voltage changes, if it is not open-circuit voltage, it does not express the charging state of the rechargeable battery 10 correctly. The open-circuit voltage detector 71 outputs the detected open-circuit voltage value to the conversion machine 72.

[0029]The relation of open-circuit voltage and a charging state of the rechargeable battery 10 whose conversion machine 72 in the standard charging state set part 70 is memorized. [ like drawing 2 mentioned above ] According to this relation memorized, the conversion machine 72 is outputted to the integrator 52 which converts the inputted open-circuit voltage value into the charging state value of the rechargeable battery 10, and the charging state primary detecting element 50 has by making the converted charging state value into a standard charging state value. The relation shown in drawing 2 is a relation about cell 1 cell, and when making a rechargeable battery in-series and using it for some as a cell group, it should just make the relation which made the value which multiplied by the number connected in series the open-circuit voltage value memorize. Two or more open-circuit voltage detectors can be used, the open-circuit voltage of each rechargeable battery can be detected, and it can also be considered as the standard charging state value of the rechargeable battery 10 by making the

average value into an open-circuit voltage value according to the relation in the case of the rechargeable battery of one cell.

[0030] This charge-and-discharge control system may carry out standard charging state setting out once before operation starts, such as vehicles, apparatus, etc. carried or equipped, or after actuation finishing, and when operating time is long and an operation is once suspended [ and ] during an operation, it may carry out at any time. By performing standard charging state setting out frequently, the charging state of the more exact rechargeable battery 10 can be grasped.

[0031] <Nonaqueous electrolyte secondary battery> The nonaqueous electrolyte secondary batteries which the charging and discharging control device of this invention makes the object of control are a nonaqueous electrolyte secondary battery which has the anode which used the lithium transition metal multiple oxide as positive active material, and what is called a lithium secondary battery. In the lithium transition metal multiple oxide which can be used as positive active material. For example, the regular arrangement stratified halite structure lithium cobalt multiple oxide which can constitute a 4V class rechargeable battery, Various things including regular arrangement stratified halite structure lithium nickel complex oxide, a regular arrangement stratified halite structure lithium manganese multiple oxide, a Spinel structure lithium manganese multiple oxide, etc. are mentioned. Also in these, a regular arrangement stratified halite structure lithium cobalt multiple oxide, Three sorts of things of regular arrangement stratified halite structure lithium nickel complex oxide and a regular arrangement stratified halite structure lithium manganese multiple oxide, It is having the same crystal structure, and it has a crystal structure dramatically stabilized to the occlusion and discharge of lithium of 50% or less of quantity of theoretical capacity so that it may clarify by the paragraph of a next example. If this point is taken into consideration, to the nonaqueous electrolyte secondary battery used as the controlled object of the charging and discharging control device of this invention, it is desirable to use any one sort or two sorts or more of mixtures as positive active material among three sorts of these things.

[0032] As for a regular arrangement stratified halite structure lithium cobalt multiple oxide, a stoichiometric composition is expressed with  $\text{LiCoO}_2$ . What is expressed with empirical formula  $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$  which replaced a part of site of Co atom other than this stoichiometrical thing of a presentation by the atom of other elements (M), such as Li, aluminum, and other transition metals, and aimed at stability of the crystal structure can be used for positive active material. Similarly to regular arrangement stratified halite structure lithium nickel complex oxide. What is expressed with  $\text{LiMnO}_2$  and  $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$  by the regular arrangement stratified halite structure lithium manganese multiple oxide in what is expressed with empirical formula  $\text{LiNiO}_2$  and  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  can be used.

[0033]Incidentally, the theoretical capacity per unit weight of  $\text{LiCoO}_2$  is 274 mAh/g,  $\text{LiNiO}_2$  is 283 mAh/g and  $\text{LiMnO}_2$  is 286 mAh/g. The anode theoretical capacity of nonaqueous electrolyte 2 cell which used these for positive active material serves as a value which multiplied the theoretical capacity per above-mentioned positive-active-material unit weight by the amount of the positive active material used, and should just perform charge and discharge by making this value into anode theoretical capacity in charge and discharge control in the field equivalent to 50% or less of that capacity.

[0034]Generally, the nonaqueous electrolyte secondary battery is using an anode, a negative electrode, a separator, nonaqueous electrolyte, etc. as the main components, and follows a nonaqueous electrolysis rechargeable battery also with a common nonaqueous electrolyte secondary battery used as the controlled object of the charging and discharging control device of this invention. Hereafter, these main components are explained briefly. An anode mixes a conducting material and a binder to the above-mentioned lithium transition metal multiple oxide as positive active material, A suitable solvent is added if needed, and what was used as paste state anode laminated wood is applied to collector surfaces, such as a product made from aluminium foil, and it dries, and can form by raising active material density with a press after that.

[0035]The conducting material used for an anode is for securing the electrical conductivity of a positive active material layer, and what mixed one sort of carbon substance powdery parts, such as carbon black, acetylene black, and black lead, or two sorts or more can be used for it. The binder can play the role which ties an active material particle, and thermoplastics, such as fluorine-containing resin, such as polytetrafluoroethylene, polyvinylidene fluoride, and fluorocarbon rubber, polypropylene, and polyethylene, can be used for it. As a solvent which distributes these active materials, a conducting material, and a binder, organic agents, such as N-methyl-2-pyrrolidone, can be used.

[0036]Metal lithium, a lithium compound, etc. can be used for a negative electrode. Also when metal lithium etc. are used for a negative electrode, and the problem of the deposit of the dendrite to a negative electrode surface arises, it is desirable to use for negative electrode active material occlusion and the carbon material which can be emitted for a lithium ion, and to make a negative electrode constitute from a certain thing. As a carbon material which can be used, powdery parts, such as organic compound baking bodies, such as natural graphite, an artificial graphite, and phenol resin, and corks, are mentioned. In this case, a binder is mixed to negative electrode active material, spreading desiccation can be carried out on the surface of charge collectors, such as a product made from copper foil, and what added the suitable solvent and was used as paste state negative-electrode laminated wood can be formed.

[0037]As a negative-electrode binder in this case, like an anode, although organic solvents, such as N-methyl-2-pyrrolidone, can be used as a solvent, fluorine-containing resin, such as

polyvinylidene fluoride, etc., One sort or two sorts or more of the cellulose ether system substances and styrene-butadiene-rubber latex which replace with these things and are chosen from groups, such as methyl cellulose and carboxymethyl cellulose, as a binder, Water can also be used as a solvent using a compound binder with synthetic rubber system latex type adhesives, such as carboxy denaturation styrene-butadiene-rubber latex.

[0038]A separator is made to fasten between an anode and a negative electrode. It can hold an electrolysis solution, and can pass ion, a separator isolating an anode and a negative electrode, and thin fine porous membrane, such as polyethylene and polypropylene, can be used for it. Nonaqueous electrolyte dissolves lithium salt in an organic solvent as an electrolyte. As an organic solvent, an aprotic organic solvent, for example, ethylene carbonate, One sort or these two sorts or more of mixed liquor, such as propylene carbonate, dimethyl carbonate, diethyl carbonate, gamma butyrolactone, acetonitrile, dimethoxyethane, a tetrahydrofuran, dioxolane, and a methylene chloride, can be used. As lithium salt in which it is made to dissolve,  $\text{LiI}$  which produces a lithium ion,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ , etc. can be used by making it dissolve.

[0039]The shape can be made into various things, such as a lamination type and cylindrical, although it is a nonaqueous electrolyte secondary battery which comprises the above thing. Even if it is a case where which shape is taken, a separator is made to fasten to an anode and a negative electrode, As it winds around lamination or rolled form by turns, is considered as an electrode body and can be made to be able to flow through the between to the positive pole terminal and negative pole terminal which pass outside from an anode and a negative electrode, respectively, this electrode body can be sealed to a cell case with nonaqueous electrolyte, and a cell can be completed. It is also possible for it to be also controllable by 1 cell independent, and for it to be in-series or parallel, to combine two or more rechargeable batteries, and to control the completed rechargeable battery by the charging and discharging control device of this invention in one as a cell group.

[0040]

[Example]The charge-and-discharge-control method of the nonaqueous electrolyte secondary battery of this invention can make capacity deterioration of nonaqueous electrolyte very small by carrying out charge and discharge in the field of 50% or less of anode theoretical capacity. A value called 50% of anode theoretical capacity is a value which the artificer verified by various examinations. Below, a \*\*\*\* examination is explained as an example for this verification.

[0041]<Production of a nonaqueous electrolyte secondary battery> In this example, the nonaqueous electrolyte secondary battery which used the lithium nickel complex oxide of regular arrangement stratified halite structure for positive active material, and used the artificial graphite for negative electrode active material was produced. Hereafter, production of this

rechargeable battery is explained. The anode adjusted anode laminated wood and produced the sheet shaped thing by carrying out coating of this anode laminated wood to a charge collector. To first, the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{aluminum}_{0.05}\text{O}_2$  (product made from Fuji chemicals: LINILITE CA-5) 90 weight section as an active material. As a conducting material, acetylene black (DENKI KAGAKU KOGYO make: HS-100) 5 weight section, Polyvinylidene fluoride (Kureha Chemical Industry make: KF polymer) 5 weight section was mixed as a binder, optimum dose of N-methyl-2-pyrrolidone was added as a solvent, it fully kneaded, and paste state anode laminated wood was obtained. This anode laminated wood was applied to both sides of a 20-micrometer-thick aluminium foil charge collector, and it dried, and compressed in the roll press after that, and the sheet shaped anode was produced. The size of the anode was 54 mm x 450 mm, and anode laminated wood layer thickness could be 40 micrometers per one side.

[0042]The negative electrode also adjusted negative-electrode laminated wood, and produced the sheet shaped thing by carrying out coating of this negative-electrode laminated wood to a charge collector. [ as well as an anode ] To first, artificial-graphite (made in Osaka Gasquet Michal: MCMB25-28) 95 weight section as an active material. Polyvinylidene fluoride (Kureha Chemical Industry make: KF polymer) 5 weight section was mixed as a binder, optimum dose of N-methyl-2-pyrrolidone was added as a solvent, it fully kneaded, and paste state negative-electrode laminated wood was obtained. Like the anode, this negative-electrode laminated wood was applied to both sides of a 10-micrometer-thick copper foil charge collector, and it dried, and compressed in the roll press after that, and the sheet shaped negative electrode was produced. The size of the negative electrode was 56 mm x 500 mm, and negative-electrode laminated wood layer thickness could be 50 micrometers per one side.

[0043]The separator made from polyethylene (the product made from TONEN TARUPISU: 25-micrometer thickness, 58-mm width) was made to fasten among both, the above-mentioned anode and the negative electrode were wound around rolled form, and the electrode body was made to constitute. Subsequently, insert this electrode body into an 18650 type cylindrical battery can, and the nonaqueous electrolyte made to dissolve  $\text{LiPF}_6$  in the mixed solvent with which the volume ratio 1:1 was made to mix ethylene carbonate and diethyl carbonate by the concentration of 1M is poured in, After impregnating with an electrode body, it sealed by crimping a top cap and the cylindrical nonaqueous electrolyte secondary battery was completed.

[0044]<Evaluation of the cycle characteristic by various charge-and-discharge conditions> The cycle test which repeats charge and discharge on various charge-and-discharge conditions after aging for one week with a room temperature was done to the above-mentioned nonaqueous electrolyte secondary battery, and the cycle characteristic of this rechargeable battery was evaluated. The adopted charge-and-discharge conditions the environmental

temperature on which a rechargeable battery is put at 20, 30, 40, 50, and 60 °C. \*\*/discharge final voltage to 4.2/3.0, 4.1/3.0, 4.0/3.0, 4.2/3.2, 4.2/3.1, and 4.1/3.1V. \*\*/discharge current density was set as 0.5/0.5, 1.0/1.0, and 2.0/2.0mA/[cm]<sup>2</sup>, \*\*/discharging method was set as constant current constant potential charge / constant current discharge, and constant current charge/constant current discharge, respectively, and it was considered as the conditions of a large number which combined these various conditions. The number of cycles was made into 100 to 500 cycle.

[0045]The initial service capacity at the time of the start of a charge-and-discharge cycle test and the service capacity at the time of an end were measured, respectively, and the degradation rate of the service capacity per 1 cycle was searched for from the following formula.

The relation between initial service capacity and a degradation rate is shown in drawing 4 per  $(100 - (\text{service capacity} / \text{initial service capacity at the time of the end of 100 cycles})) / \text{number positive-active-material unit weight of cycles}$ . It turns out that initial service capacity is so large that the environmental temperature on which a rechargeable battery is put at the time of a cycle test is high so that clearly from the result of drawing 4. This is understood to be for the internal resistance of a rechargeable battery to decrease by factors, such as a viscosity decrease of nonaqueous electrolyte, in connection with a rise in heat. However, even if drawing 4 is a case where which conditions of environmental temperature, \*\*/discharge final voltage, \*\*/discharge current density, and \*\*/discharging method are changed, it has a relation with a linear degradation rate of initial service capacity and service capacity, and has suggested that a degradation rate is dependent only on initial service capacity.

[0046]When the straight line in drawing 4 in which the relation between initial service capacity and a degradation rate is shown was extrapolated and service capacity is restricted to 140 mAh/g, it is thought that cycle degradation may become zero. That is, restricting service capacity will restrict into an anode the quantity of the lithium ion which repeats occlusion and discharge, I hear that the cycle degradation resulting from positive active material becomes zero, and it has it. Incidentally a value called these 140 mAh/g is equivalent to about 50% of 283 mAh/g which is the theoretical capacity of the lithium nickel complex oxide used as positive active material. Therefore, by the same principle, if it is the nonaqueous electrolyte secondary battery which used the lithium transition metal multiple oxide with the same crystal structure of regular arrangement stratified halite structure as positive active material, if charge and discharge are repeated in 50% or less of field of theoretical capacity, service capacity will be presumed to hardly deteriorate.

[0047]<Cycle characteristic by the amount charge and discharge of constant volume> That the above-mentioned theory should be verified, the cycle test which repeats the amount charge and discharge of constant volume (charge and discharge which set constant quantity of

electricity by which charge and discharge are carried out) was done on the above-mentioned nonaqueous electrolyte secondary battery, and the cycle characteristic was evaluated to it. Constant current discharge of the conditions of the amount charge and discharge of constant volume shall be carried out until it charges by the constant current of current density  $1.0 \text{ mA/cm}^2$  under 60 °C environmental temperature and becomes the capacity of 140 mAh/g by the same current density  $1.0 \text{ mA/cm}^2$ . Charge final voltage was set as 4.2, 4.1, 4.0, and 3.9V, and did the cycle test to 1000 cycle about the thing of each charge final voltage condition. [0048]The cycle test of two conditions of performing constant current charge/constant current discharge fixed °C / discharge final voltage 4.1/3.0, and in 4.0/3.0V was also done by °C / discharge current density  $1.0/1.0 \text{ mA/cm}^2$  for comparison. The cycle characteristic of the case in the amount charge and discharge of constant volume and the cycle characteristic of the case in the charge and discharge performed in the fixed charge-and-discharge-voltage range are shown in drawing 5.

[0049]When charge and discharge are repeated in the range of °C / discharge final voltage 4.1/3.0V so that drawing 5 may show, Although there was about 170 mAh/g in initial service capacity, service capacity decreased linearly and decreased at last after 1000 cycles even at about 40 mAh/g as the cycle was piled up. Although there was about 160 mAh/g in initial service capacity also when charge and discharge were repeated in the range of °C / discharge final voltage 4.0/3.0V, service capacity decreased linearly too and decreased after 1000 cycles even at about 70 mAh/g as the cycle was piled up. On the other hand, the thing which carried out charge and discharge in the amount of constant volume of 140 mAh/g, At the time of 1000 cycles, anything of the conditions that charge final voltage is 4.2, 4.1, 4.0, and 3.9V could continue maintaining the capacity, and it became clear that it is in the state which can increase the number of cycles also after that.

[0050]Next, the average discharge voltage of the case in the amount charge and discharge of constant volume and the case of the charge and discharge performed in the fixed charge-and-discharge-voltage range is compared. In the charge and discharge performed in the charge-and-discharge-voltage range to which the two above-mentioned condition was fixed, a thing 3.65-3.6 V in average discharge voltage was falling even to 3.4-3.3V after the end of 1000 cycles in early stages of the cycle test. On the other hand, the early average discharge voltages of what performed the amount charge and discharge of constant volume are 3.8, 3.75, 3.7, and 3.6V, respectively about the thing of the monograph affair in which charge final voltage is 4.2, 4.1, 4.0, and 3.9V.

Anything of charge final voltage conditions remained in the fall of an about [ 0.05V ] also after the end of 1000 cycles.

When it restricted to 50% or less of anode theoretical capacity and charge and discharge were

performed in the amount of constant volume also from the thing here, it became clear that a rechargeable battery has hardly deteriorated.

[0051]When the average service capacity to 1000 cycle is measured, the thing at the time of repeating charge and discharge in the range of \*\* / discharge final voltage 4.1/3.0V 105 mAh/g, What performed the amount charge and discharge of constant volume serves as 140 mAh/g to the things at the time of repeating charge and discharge in 4.0/3.0V being 115 mAh/g.

Therefore, the average service capacity in the cycle became clear [ also increasing conversely ] over a long period of time by carrying out the charge and discharge which stopped service capacity a little. When this is converted into an energy density, in order to multiply by the difference of the average discharge voltage mentioned above in addition to an average service capacity difference, the predominance of the amount charge and discharge of constant volume suppressed in 50% or less of capacity of anode theoretical capacity becomes still larger.

[0052]If the above result is synthesized, most capacity deterioration of a rechargeable battery can be prevented by controlling the nonaqueous electrolyte secondary battery which used the lithium transition metal multiple oxide as positive active material to perform charge and discharge in the field of 50% or less of anode theoretical capacity. 50% or less of field of anode theoretical capacity since the almost same result is brought in any [ which was performed by changing charge final voltage in the amount charge and discharge of constant volume ] case, When it was in the chargeable and dischargeable field reversibly, whether it is a field near the full charge state side or was a field near the empty charging state side, it became clear [ that there is also no difference in the preventive effect of capacity deterioration ].

[0053]

[Effect of the Invention]The charging and discharging control device of this invention the nonaqueous electrolyte secondary battery which has the anode which used the lithium transition metal multiple oxide as positive active material, It is a charging and discharging control device which carries out charge and discharge in the field which monitors the charging state of this rechargeable battery by monitoring charge-and-discharge quantity of electricity, and is equivalent to 50% or less of capacity of anode theoretical capacity. This charging and discharging control device which can enforce such a control method becomes possible [ making very small degradation of the cell capacity of the nonaqueous electrolyte secondary battery by the charge and discharge repeated ].

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[Translation done.]